Thermodynamic Relations Along
the Principal Hugoniot

by Steven B. Segletes

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Steven B. Segletes
Weapons and Materials Research Directorate, ARL

Abstract

Some thermodynamic relations are derived along the principal Hugoniot of materials for which the Grüneisen relation is a function of volume only. Rather than being expressed in terms of traditional thermodynamic variables, such as volume and temperature, the relations are expressed in terms of the shock-Hugoniot behavior and of a term grouping that is related to the Grüneisen function. By so doing, a new perspective is gained on both the nature of the Hugoniot as well as the interrelation of thermodynamic quantities along the Hugoniot.

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Table of Contents

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1. Background

Thermodynamic relations are traditionally expressed in terms of standard thermodynamic state variables, such as volume and temperature. In this report, we examine the thermodynamics of solids along the principal Hugoniot of the material. We break from the traditional approach, however, and express the behavior of thermodynamic paths through the Hugoniot [in the pressure-volume (p,V) and energy-volume (E,V) planes] in terms of the the behavior of the Hugoniot itself and a term grouping that is related to the Grüneisen function, $\Gamma = V(\partial p/\partial E)_V$. In this study, we consider only materials for which $\Gamma = \Gamma(V)$ alone.

The equation of state traditionally expresses pressure in terms of volume and temperature, or alternately in terms of volume and internal energy (if the specific heat behavior is known). For the modeling of solids, the so-called Grüneisen form, whereby $\Gamma = \Gamma(V)$ and $p = p(E,V)$, has been widely accepted to model material behavior (in the absence of phase changes) over pressures into the megabar range. In this form, the pressure and energy at arbitrary states are related back to conditions along a reference path of known thermodynamic characteristics (denoted by subscript "*ref*"):

$$p - p_{ref} = (E - E_{ref})/\psi \quad , \tag{1}$$

where the variable ψ is given by $\psi = V/\Gamma = (\partial E/\partial p)_V$. In this equation, E and V denote the specific energy and specific volume, respectively. If the equation-of-state reference curve is taken as the principal Hugoniot (the Hugoniot originating at zero temperature and pressure), where the Rankine-Hugoniot shock-energy relation governs, given by

$$E_h = p_h (V_0 - V)/2 \quad , \tag{2}$$

then eqns (1) and (2) may be combined, eliminating E_h, to yield

$$p - E/\psi = p_h [1 - (V_0 - V)/(2\,\psi)] \quad . \tag{3}$$

With the Hugoniot as the equation-of-state reference function, this form of the equation of state

1

is defined only where the p_h function is defined—namely, between the reference volume, V_0, and a limiting compressive volume at which the Hugoniot asymptotes to infinite pressure. The thermodynamic study of material behavior along the principal Hugoniot is, in and of itself, important, since the vast majority of experimental shock data obtained lie along this curve. Additionally, because most hydrocode implementations of the equation of state are given explicitly by the Hugoniot-based eqn (3), a pedagogical study of this equation form is further warranted.

We introduce the nondimensional variable z to denote the quantity

$$z = (V_0 - V)/(2\,\psi) \ , \tag{4}$$

which appears on the right-hand side of eqn (3). In terms of more traditional equation-of-state variables, z may be expressed as

$$z = \Gamma\mu/2 \ , \tag{5}$$

where the compression, μ, is defined as $\mu = (V_0 - V)/V$. This variable, z, will prove to be a convenient term grouping in which to express subsequent results. Whereas ψ may be thought of as a specific volume, scaled by a factor of $(1/\Gamma)$, the variable, z, on the other hand, may be thought of as the nondimensional compression, scaled by a factor of $(\Gamma/2)$. Thus, in terms of z, the Hugoniot-based equation of state is given as

$$p - E/\psi = p_h(1-z) \ . \tag{6}$$

Note that, under the assumption that $\Gamma = \Gamma(V)$, the right-hand side of this equation remains a function of volume only. Within the range of validity of the model and data, eqn (6) may be used to model all valid thermodynamic states of a material, on or away from the Hugoniot reference curve.

2

2. The Behavior of z

We may learn something of the limiting behavior of z by studying eqn (6). At large enough compressions, the Hugoniot will asymptote vertically toward infinite pressure [since electronic effects cannot be modeled within the $\Gamma(V)$ assumption]. At the specific volume corresponding to this Hugoniot asymptote, call it V_x, the zero-temperature isotherm is a well-behaved, finite-valued function—thus, $p_c(V_x)$ and $E_c(V_x)$ are bounded (where the subscript "c" denotes conditions along the zero-temperature isotherm). Similarly, Γ_x and thus ψ_x are nonzero and finite, as well. Examining eqn (6) at the zero temperature state then, the left-hand side of the equation is finite and bounded. With p_h at this specific volume being infinite, the equation can only hold true if $z \rightarrow 1$ at the specific volume associated with the asymptotic state of the Hugoniot. On the other hand, at the reference, unshocked state, where V equals V_0, the compression and thus the value of z are both identically zero.

Thus, for the limits of unshocked and infinitely shocked states, the value of the z variable takes on values of 0 and 1, respectively. For shock strengths in between these asymptotic states, Segletes [1] showed, with his Mode II criterion, that $0 < \Gamma < 2/\mu$ is a requirement for thermodynamic stability of any material for which $\Gamma = \Gamma(V)$. Expressed in terms of z, this relation is simply

$$0 < z < 1 \;, \tag{7}$$

showing that, indeed, the value of z at V_x and V_0 bounds the behavior of z between V_x and V_0.

We now inquire as to whether the variable z behaves monotonically between these limiting conditions. We proceed by differentiating, with respect to V, the value of z given in eqn (4), which yields

$$z' = -(1/\psi)(1/2 + z\,\psi') \;. \tag{8}$$

Since ψ and z are always positive for shock compression, the behavior of z' hinges on that of ψ'. Segletes previously showed [2] that, as a requirement to avoid so-called Rayleigh-slope

3

instabilities, the criterion $\psi' \geq -1$ needs to be satisfied. The violation of this criterion can produce, for shocks originating at elevated temperatures, a postshock pressure below the preshock pressure—clearly, a nonsensical result. Adherence to the $\psi' \geq -1$ criterion would guarantee the monotonicity of z (i.e., $z' < 0$) for the domain $0 \leq z < 1/2$. Segletes later showed [3] that, from the consideration of isobaric expansions at high pressure, a stricter condition, $\psi' \geq 0$, was applicable for $\Gamma(V)$ materials. This stricter condition, in light of eqn (8), would guarantee z-monotonicity at all specific volumes, and is a particularly relevant constraint in the domain $1/2 \leq z \leq 1$, which corresponds to conditions of high compression and temperature along the Hugoniot. Thus, under the assumption of a material for which $\Gamma = \Gamma(V)$, to which we limit this discussion, the monotonicity of z follows from results previously established [2, 3]. Though this monotonicity is established for $\Gamma(V)$ materials over the complete Hugoniot, the practical limitations of the $\Gamma(V)$ assumption (for which these results were derived) is limited, for many solids, to a pressure range of several megabars.

3. Isentropic Behavior Near the Hugoniot

To begin our examination of thermodynamic behavior along the Hugoniot, we begin with the isentrope. Starting with the shock form of the equation of state, eqn (6), differentiate along an isentrope, to obtain

$$\left(\partial p / \partial V\right)_s = -p_h z' + p_h'(1-z) + \frac{\psi\left(\partial E / \partial V\right)_s - E\,\psi'}{\psi^2} \ . \tag{9}$$

Knowing that $\left(\partial E / \partial V\right)_s = p$, one may evaluate eqn (9) along the Hugoniot (i.e., along an isentrope where it intersects with the Hugoniot), such that p and E take on values of p_h and E_h, respectively, while the expression $\left(\partial p / \partial V\right)_{s,h}$ is used, here, to denote the slope of the isentrope through a point on the Hugoniot. One may eliminate the Hugoniot internal-energy term by substituting the shock energy relation, eqn (2), expressed in z as $E_h = p_h \psi z$, to obtain the result

$$\left(\partial p / \partial V\right)_{s,h} = p_h'(1-z) - \frac{p_h}{\psi}\left(1 + z\psi' + \psi z'\right) \ . \tag{10}$$

4

The product differentiation rule may be employed to combine the terms $(z\psi' + \psi z')$ into $(z\psi)'$. The product, $z\psi$, is simply $(V_0 - V)/2$, and thus its derivative is $-1/2$. Simplification gives

$$\left(\partial p/\partial V\right)_{s,h} = p_h'(1-z) - \frac{p_h}{2\psi} \quad . \tag{11}$$

This equation relates the slope of an isentrope at a point on the Hugoniot to the slope of the Hugoniot and the value of the Hugoniot pressure. To interpret this equation, so as to better understand the variable z, multiply by -1 and substitute the definition of z, eqn (4), into the last term to obtain

$$-\left(\partial p/\partial V\right)_{s,h} = -p_h'(1-z) + \frac{p_h}{(V_0-V)}z \quad . \tag{12}$$

The left-hand side is the slope, in (p,V) space, of the isentrope through a point on the Hugoniot. It is expressed as a linear combination, in z, of two terms: the slope of the Hugoniot itself at that point, and the slope of the Rayleigh line through the point and the Hugoniot origin. The negative signs were used to keep the physical magnitudes of these slopes positive. Using the terms H, I, and R to respectively represent the slopes of the Hugoniot, isentrope, and Rayleigh line through the given Hugoniot point (see Figure 1), the expression may be restated as

$$I = H(1-z) + Rz \quad . \tag{13}$$

Because z remains between 0 and 1, the value of I may be thought of as a weighted average of H and R. Not only does this equation, therefore, reinforce our understanding that the isentropic slope on the principal Hugoniot must lie between the Rayleigh and Hugoniot slopes (i.e., $H > I > R > 0$, used by Segletes [1] to prove his Mode II criterion), but it also demonstrates that the variable z is intimately related to these slopes and to the disturbance velocities that these slopes engender. For example, at large compressions, where the Hugoniot slope, H, approaches unbounded values, ideal gas limits tell us that the isentropic slope, I, at a given volume, can be

shown proportional to pressure. The Rayleigh slope, R, also has this pressure proportionality, by definition. Thus, in the high-pressure limit, even though p_h becomes unbounded, the ratio I/R remains finitely bounded. The only way that this condition can hold with H becoming unbounded is that, not only must $z \to 1$, but z must functionally approach unity such that $H(1-z)$ remains bounded, as well. By contrast, at the low end of the shock-compression spectrum ($z<<1$), eqn (13) indicates that the isentrope is approximated by the Hugoniot—a well known fact, but one which is made functionally clear from the structure of eqn (13) knowing, further, that at $z \approx 0$, $R \approx H$.

4. Thermodynamic Relations in Terms of H and R

An important relationship relating the isentropic slope, I, to the Hugoniot (characterized by H and R), in terms of the z variable, was derived in eqn (13). Realizing that slopes R and H are specified by a given Hugoniot point and its (p,V)-slope, an intrinsic linkage between the Hugoniot and Grüneisen function becomes undeniably apparent. Other thermodynamic paths through points on the Hugoniot may be similarly expressed in terms of H, R, and z. Consider the thermodynamic change along a infinitesimal path of arbitary slope $-m$, in (p,V) space [i.e., define the path such that $(\partial p/\partial V)_m = -m$]. It may be shown from eqn (6) that

$$-\left(\partial p/\partial V\right)_m \psi + \left(\partial E/\partial V\right)_m = -p_h/2 - p_h'\psi(1-z) + (p-p_h)\psi' \quad . \tag{14}$$

At points on the principal Hugoniot, the last term becomes identically zero. Were one to study material states off of the principal Hugoniot, this last term of eqn (14) should be retained. We restrict, however, the current analysis to the Hugoniot and thus discard the term. Employing the definitions of H and R used earlier, and substituting $-m$ for the (p,V)-slope in question, eqn (14) becomes, along the Hugoniot,

$$m\psi + \left(\partial E/\partial V\right)_m = \left[H(1-z) - Rz\right]\psi \quad . \tag{15}$$

This equation is actually of a general form, from which a result like eqn (13) may likewise be obtained. This equation may be used to study not only volume derivatives of pressure, but

6

volume derivatives of energy, as well. In addition to using it to study the Hugoniot, isentrope, and Rayleigh-line paths, we will also use it to study the isobaric and isoenergy paths, whose negative slopes we denote with P and $\mathscr{E}$, respectively. The following additional relationships are readily established from eqn (15) (original relationships repeated for completeness):

$$H = -p_h' \, , \tag{16}$$

$$R = p_h / (V_0 - V) \, , \tag{17}$$

$$I = H(1-z) + Rz \, , \tag{18}$$

$$P = 0 \, , \tag{19}$$

$$\mathscr{E} = H(1-z) - Rz \, , \tag{20}$$

$$\left(\partial E/\partial V\right)_H = E_h' = \left[-Hz - Rz\right]\psi \, , \tag{21}$$

$$\left(\partial E/\partial V\right)_R = \left[H(1-z) - R(1+z)\right]\psi \, , \tag{22}$$

$$\left(\partial E/\partial V\right)_I = -p_h = \left[-2Rz\right]\psi \, , \tag{23}$$

$$\left(\partial E/\partial V\right)_P = \left[H(1-z) - Rz\right]\psi \, , \text{ and} \tag{24}$$

$$\left(\partial E/\partial V\right)_{\mathscr{E}} = 0 \, . \tag{25}$$

Various graphical interpretations may be inferred from these relations. In some cases, the interpretations may even be independent of z. For example, eqns (21) and (23) may be respectively expressed as

$$-\left(\partial E/\partial V\right)_H = (H + R)(V_0 - V)/2 \, , \text{ and} \tag{26}$$

$$-\left(\partial E/\partial V\right)_I = R(V_0 - V) \, . \tag{27}$$

Since the physical unit of these equations is pressure, these two relations may be graphically interpreted in (p,V) space. Figure 2 depicts the graphical construction. In the figure, R' represents the line going through the Hugoniot point of interest, but with a slope negative to that of line R (i.e., the mirror image of R about the constant-pressure line $p = p_h$). The $\partial E/\partial V$ quantities shown in the figure are magnitudes only, as the actual quantities carry a negative value.
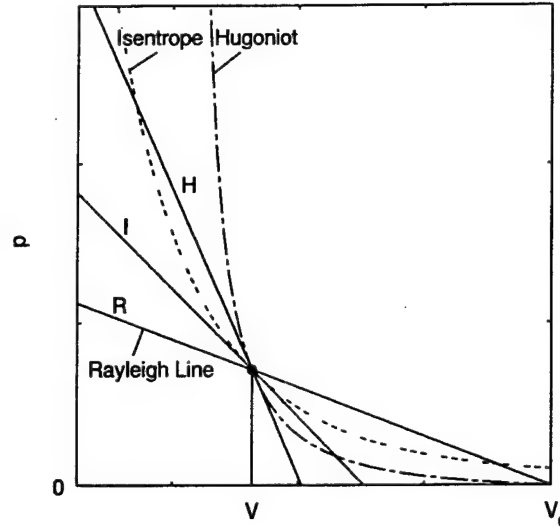
7

Fig. 1. The slopes H, I, and R, shown at a given volume, V, define the respective slopes of the Hugoniot, isentrope, and Rayleigh line through a given point on the principal Hugoniot.
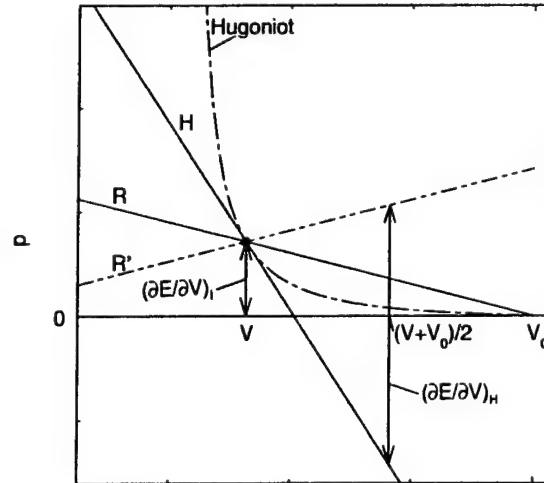

Fig. 2. A graphical interpretation of $(\partial E/\partial V)_H$ compared to that of $(\partial E/\partial V)_I$, constructed from the principal-Hugoniot curve.

8

5. Observations and Conclusions

It has been shown that the state variable, z, equal to $\Gamma\mu/2$, embodies important thermodynamic information. On the surface, it represents a measure of compression, which has been nonlinearly scaled by the factor $\Gamma/2$. Such a metric seems a natural variable for discussion of shock compression. For the weakest of shocks, its value approaches zero. In the strong-shock limit, it approaches unity. Geometrically, it may be employed to relate the properties of Hugoniots to those along other thermodynamic paths. Analytically, it behaves under constraints that are not material- or loading-path specific. The value of z, coupled with point and slope information on the Hugoniot, provide enough information to define the thermodynamics of a material. However, the algebraic simplicity by which thermodynamic changes along paths that cross the Hugoniot may be characterized, given in eqns (18)–(25), is startling and, in some cases, amenable to graphical interpretation.

Though the Grüneisen assumption $[\Gamma = \Gamma(V)]$, under which the present results were derived, can no longer be expected to hold at extremely large pressures and temperatures, it has historically been shown adequate for many materials well into the megabar shock-pressure range. Furthermore, the equation-of-state implementation in virtually all hydrocodes is based upon the $\Gamma(V)$ assumption. Thus, its study is of more than just academic interest. Because of the monotonicity of z, as shown in the current work, required of materials for which $\Gamma = \Gamma(V)$, a one-to-one correspondence must exist between z and specific volume, V. Such a correspondence, as a minimum, opens up the possibility that equations of state may be expressed more conveniently in terms of z, rather than V. There are some advantages in so doing. First, since the Grüneisen function is already embedded in the variable z, expressing an equation of state in terms of z would effectively recouple the Grüneisen function, Γ, back to the equation-of-state reference curve (*e.g.*, the Hugoniot or cold-curve). Such a coupling is important, as it has been shown [1] that arbitrary selection of a Grüneisen functional form for a given reference Hugoniot can often lead to thermodynamic inconsistency. By establishing a functional coupling between the reference curve and the Grüneisen function (even if it were empirically derived), one could check the *functional form* for thermodynamic consistency, rather than exhaustively testing every empirical combination of reference curve and Grüneisen function.

Of possible greater significance is the fact that the introduction of the variable z creates, perhaps, a framework for the development of a generic equation of state for solids in terms of primitive, macroscopic variables. This framework is possible because not only is z unit-dimensionless, but for *any* arbitrary material subject to shock loading, the value of z will proceed from zero to unity as shock strength increases. There are many approaches by which an equation of state in z might be formulated. One could specify the reference curve in terms of z directly, as in $p_h(z)$ or $E_h(z)$. Such direct specification though would likely be the result of an empirical fitting procedure. One might alternately attempt to specify the functional coupling by interrelating slopes H and R as a function of z. This latter approach is functionally equivalent to relating p_h' to p_h by way of z, or alternately E_h' to E_h by way of z. Such techniques are more amenable to analytical or semi-analytical derivation, since there do exist constraints which govern thermodynamic functions and their derivatives. Of course, the challenge here is in finding the appropriate constraint that precisely maps the derived equation of state onto the experimentally observed data.

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Steven B. Segletes

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U.S. Army Research Laboratory
ATTN: AMSRL-WM-TD
Aberdeen Proving Ground, MD 21005-5066

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Some thermodynamic relations are derived along the principal Hugoniot of materials for which the Grüneisen relation is a function of volume only. Rather than being expressed in terms of traditional thermodynamic variables, such as volume and temperature, the relations are expressed in terms of the shock-Hugoniot behavior and of a term grouping that is related to the Grüneisen function. By so doing, a new perspective is gained on both the nature of the Hugoniot as well as the interrelation of thermodynamic quantities along the Hugoniot.

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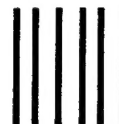**(DO NOT STAPLE)**

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